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**REPORT**

**DEVELOPMENT OF CATHODIC MATERIALS  
FOR ARCJET DEVICES**

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Contractor

**Prof. G.Burkhanov**

Business Office: **Baikov Institute of Metallurgy**  
117911 Moscow, Leninsky pr., 49  
Tel: (095) 1358701, FAX: (095) 1358680

Moscow 1995

# **DEVELOPMENT OF CATHODIC MATERIALS FOR ARCJET DEVICES**

**Principal Investigator  
Prof. G.Burkhanov**

### **List of the authors**

N.P.Lyakishev, acad. RAS  
V.A.Obukhov, dr.  
E.D.Doron'kin, dr.  
A.S.Krokhin, ing.  
V.A.Kus'mischev, dr.  
E.G.Prutskov, dr.  
V.M.Kirillova, dr.

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## INTRODUCTION

In countries with advanced science and technology it has been accumulated great experience in research and development of electrode materials for various purposes (electronics, lighting technique, electrometallurgy, welding of metallic constructions and so on) [1-3].

It was the purpose of the studies which are reported below to develop new materials for plasma-jet engine electrodes. Exploitation conditions of such electrodes are exceptionally severe: high temperatures (above  $3000^{\circ}\text{C}$ ); erosion due to plasma jet; influence of environment components, thermocycling, vibrations and etc. For this reason it is necessary to develop new resistant materials which are characterized by more high parameters and optimum chemical composition in comparison with previously developed materials for this purposes and to improve essentially (with minimum expenditure) present technologies and to develop new technologies in the field of electrode materials as well of electrode making from this new materials. Moreover it is impossible to select material with optimum chemical composition without wide testing of electrode in exploitation conditions.

From the above it is clear: that only close cooperation and communication between material scientists and designers of plasma-jet engines will lead to success.

Present report is intermediate and opens the first stage of investigation. Containing conclusions are based on results of previous investigations, of some preliminary experiments and on our foresee taking into account own results of scientific research in field of electrode materials. The first of all it does concern of single crystal production.

### Chapter 1. JUSTIFICATION OF ELECTRODE MATERIALS SELECTION

Based on analysis of plasma-jet electrode operating conditions and results of preliminary investigations to find electrode materials we concluded that tungsten can be regarded as a base of electrode materials. Tungsten show a maximum melting

point (by barometric presser) in comparison with all chemical elements (metals and nonmetals), high strength, good adsorption for alkaline and alkaline-earth metals and other advantages. But this metal is not free from disadvantages which is resolved by different methods. Increased tendency to brittle rupture is key limitation.

In the current investigation following problems have been solved:

1. increase of processing ductility and improvement of machining;
2. increase of resistance to thermocycling attack;
3. improvement of compatibility with vapour and liquid alkaline metals;
4. improvement of emissive power - rise of thermoemission current density and stabilization of thermoemitter operation;
5. increase of erosion resistance in plasma jet.

These tasks have been achieved by following methods - alloying, optimizing of powder metallurgy methods of electrode production, production of electrodes with single crystal structure.

#### 1.1. ALLOYING

In this process it has been used elements forming with tungsten substitute solid solutions or favoring to form new precipitate phases. Rhenium is most unique element which has an excellent effect on tungsten properties. Forming with tungsten solid substitute solution in wide region concentrations, rhenium sharply rises strength, including high temperature strength; ductility ("rhenium-effect"); resistance to oxidation, thermocycling action and improves emission properties. Several investigations revealed increase of work function of tungsten electrode by rhenium alloying (Table 1) [7]. Influence of rhenium on tungsten, molybdenum and another refractory metal alloy properties is in detail described in [4-6].

One significant finding is that alloying of tungsten by rhenium (up to 5 wt%) and doping by thorium - and REM-oxides increase of work function (Table 1) [2,7].

Table 1. Work function of tungsten wire (diameter 150 mkm) doped by Th- and REM-oxides (1-1,5 wt%) and alloyed by rhenium and impregnated by osmium [7]

Doping oxide . and alloying element	Work function, eV
ThO <sub>2</sub>	3.0 - 2.2
La <sub>2</sub> O <sub>3</sub>	2.96
Y <sub>2</sub> O <sub>3</sub>	3.3 - 2.96
Ce <sub>2</sub> O <sub>3</sub>	3.4 - 2.44
Nd <sub>2</sub> O <sub>3</sub>	3.88
Gd <sub>2</sub> O <sub>3</sub>	3.96
Yb <sub>2</sub> O <sub>3</sub>	4.05
ZrO <sub>2</sub>	3.97
HfO <sub>2</sub>	3.84
Re (5 wt%)	4.52
(100) single crystal	
Os	1.68
impregnated cathode	
no alloying W	4.6
(100) single crystal	

In electronics it is widely used tungsten electrodes doped by ThO<sub>2</sub> (BT-15, BT-30 and BT-50) which are characterized by low coefficient of doped diffusion, by low evaporation velocity, by high emission parameters. But toxic and radioactive ThO<sub>2</sub> demand seek a solution of ecological problems in time of organization of thorium-material production. At present time it is conducted a research concerned with replacement ThO<sub>2</sub> by La<sub>2</sub>O<sub>3</sub> (alloy BJ-10) and by Y<sub>2</sub>O<sub>3</sub> (alloys BM-15 and BM-30).

The present research covers problem of substitution of ThO<sub>2</sub> by CeO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> (partially). Alloying by Re, Os and Ir also cause the improvement of tungsten emission characteristics.

On the basis of above mentioned studies it was selected following electrode materials:



W-5 wt% ThO<sub>2</sub>  
W-2 wt% ThO<sub>2</sub>-1 wt% CeO<sub>2</sub>  
W-5 wt% Re-5 wt% ThO<sub>2</sub>  
W-5 wt% Re-1 wt% CeO<sub>2</sub>  
W-5 wt% Re-2 wt% Y<sub>2</sub>O<sub>3</sub>  
W-5 wt% Re  
W-2 wt% Os  
W-2 wt% Ir

## 1.2. SELECTION OF ELECTRODE MATERIAL PROCESS

It is known that many properties of metallic materials depend not only on character of metal-base, chemical and phase composition, but structural features: grain size, boundary extent between grains, quantity and mode of crystal defects within the grains, morphology and inclusion arrangement character and so on. This properties will be referred to as structure sensitive one. This properties determine working parameters of arc, operating engine characteristics and technological electrode process (for example mechanical properties, erosion resistance).

For refractory metals (especially for tungsten), high mechanical properties can be achieved by forming of fine dispersed or single crystal structure. Coarse structure of tungsten and its alloys results in the sharp embrittlements. Fig.1 shows ductility of tungsten as a function of grain size.

Dispersed Th- and REM-oxides inclusions and Re (as substitute element) facilitate the formation of fine-grained structure, although reduction in size of grains by the action of dope element oxide particles and metallic alloying elements proceeds by different mechanisms. It is important to note that alloying must not to result the formation of oxide- and carbide inclusions out of C- and O-impurities.

Such inclusion-induced embrittlement may be overlap the effect of ductility increase out of grain reduction in size.

It is known that not only chemical and phase composition but process method determine character of material structure. As a rule for production of electrode materials for various purposes in particularly cathode materials powder metallurgy methods are used.

These methods allow to form fine-grained structure with homogeneous distribution of oxide inclusions and to introduce these oxides over wide concentration ranges.

It is necessary to note that excessive reduction in size of grains results in the drop of electrode operating characteristics. According to [8] excessive fine grain structure of W-ThO<sub>2</sub> cathodes (for xenon lamp of superhigh pressure) results in the acceleration of Th-depletion and as a consequence in the emission decrease and in acceleration of cathode erosion. For this reason fabrication route has been optimized and corrected: powders of different degree of dispersion have been used, special regimes of mixing, pressing and sintering in reducing atmosphere have been selected.

Anode materials - W-Re, W-Os, W-Ir (without oxide particles as dope) have been obtained by melting followed by crystallization from liquid phase.

5 wt% Re-, Os- and Ir-content limitation in tungsten can be explained by features of property changes as function of composition and by economical reasons. At the same time 5 wt%-alloying element content in tungsten afford required level of material properties which determine operating parameters and high adaptability to manufacture.

## Chapter 2. SELECTION OF ELECTRODE MATERIAL PROCESS

### 2.1. PRODUCTION OF CATHODE MATERIALS

In present work cathode materials of following compositions have been produced:

W-5 wt% ThO<sub>2</sub>

W-2 wt% ThO<sub>2</sub>-1 wt% CeO<sub>2</sub>

W-5 wt% Re-5 wt% ThO<sub>2</sub>

W-5 wt% Re-1 wt% CeO<sub>2</sub>

W-5 wt% Re-2 wt% Y<sub>2</sub>O<sub>3</sub>

Tungsten powder (grade B4-5 with bulk weight 3.6 g/cm<sup>3</sup>) have been used as a base material. Impurity content is following (wt%): K - 0.01; Al - 0.001; Fe - 0.005; Ca - 0.002; Mo - 0.01; Ni - 0.001; Si - 0.02.

Tungsten doped by Th- and Ce- oxides have been produced by mixing of tungsten powder with oxides, by screening and plasticizing, by pressing of bars (12x12x450 mm). Heat treatment of bars included low temperature sintering (1200°C) and high temperature sintering (2000°C - I stage and 2500°C - II stage) followed by swaging (1500-1600°C) of bars and turning of rods to finished size.

Feature of cathode material containing Re is following: tungsten powder is alloyed with rhenium in the form of ammonium perrhenate powder followed by reducing in H<sub>2</sub>-atmosphere. Further W-Re powder is doped by ThO<sub>2</sub> and CeO<sub>2</sub>. Finished cathodes have been produced by above mentioned way.

Initial material (in form of a rod) for growing of W-Re, W-Os, W-Ir single crystals have been produced by the same way too.

## 2.2. PRODUCTION OF ANODE MATERIALS

In the current investigation tungsten and its alloys with Re, Ir and Os in area of substitute solid solution have been selected for growing of refractory single crystals. Formation of solid solutions is the most effective method of property improvement of metal by melting. For tungsten-base material this method is the most promising owing to tungsten ability to form with many transition metals (including Re, Os and Ir) wide areas of substitute solid solutions.

Increase of alloying element content in tungsten results not only in improvement of electrode requirement operating characteristics, but in decrease of technological ductility, in impede of machining, in decrease of electrode output and service life. Re is exception. Production of single crystals with low gas impurity content not only solves the problem of material brittleness and of requisite physical properties, but permits to control by properties owing to theirs orientation dependence.

For growing of refractory metal single crystals zone-refining method with using of electro-beam heating have found a wide application in the laboratory and the technological practice. This method permits to maintain the high temperature

heating and to control the process of melting easily.

Various modifications of this method have come to light in recent years [5,9].

The principle of the method is described in Fig.2. Melting of metals occurs by the heating of sample through high power electron flux action. For protection of sample against contamination special cathode device have been designed. It carries fine focusing of electron flux and excepts reciprocal contamination of heating source and melting sample. The design provides for a stabilization of zone-refining melting parameters.

Quality of refractory metals single crystals (purity, structure perfection, homogeneous distribution of alloying component and impurities) depends on purity of initial material, vacuum degree, regime of zone melting (number of melting zone passes along sample, melting zone width, change in zone width from pass to pass).

A promising method of growing single crystal of refractory metals uses a low-temperature plasma [10] allowing the growth of large refractory metal single crystals (for example those of tungsten with diameter of up to 50 mm), as well an effective purification from number of impurities: C, O, Si, P, S, Cr, Mn, Fe, Al and so on.

The principle of the method is described in Fig.3. The idea of the method is the follow: the original single crystal seed of tungsten (5) is placed on top of the water-cooled copper rod, moving upwards and downwards along the vertical axis. The plasmotron (2) is mounted on the upper flange of the operating chamber co axially with seed. The single crystal seed is used as the anode (5), while the  $W-Y_2O_3$ -electrode of the plasmotron is the cathode (1). Electric arc (7) is excited between cathode of plasmotron and single crystal seed anode. The inert gas, passing through plasmotron (argon, helium, hydrogen and their mixtures) simultaneously ensures a protective atmosphere for the specimen.

The process of single crystal growth starts by melting the upper part of the seed crystal (4) by the plasma arc. From one side tungsten rod-initial material (3) is fed. The liquid-metal bath (4) which forms is steadily fed by molten drops (6) from the same time the seed secured on the rod moves down, keeping the

liquid-solid interface at a constant level. The argon-helium mixture can be considered the most suitable media to generate the plasma for growing tungsten and its alloys single crystals.

Carbon and sulfur are removed most effectively. Their content is ten times as little in comparison with zone-refining single crystals. Each remelting causes the decrease of C-content two times as little in spite of C-content in initial tungsten rods. P, Si, Fe are removed less effectively. Effectiveness of tungsten purification after double remelting is demonstrated by data of Table 2.

Table 2. Reduction of impurity content after double plasma-arc remelting (at%  $10^{-4}$ )

Impurity	Initial tungsten	Single crystal (double remelting)
C	321	0.15
O	11.4	0.115
Mo	945	817
Cr	3.18	0.318
Fe	108	77.8
Ti	7.64	5.74
Pb	2.66	0.887
Si	25.6	19.3
P	155	56.6
Sn	6.18	1.55
Ni	5.0	2.5
S	54.7	54.7
Cu	5.76	2.89
Al	33.1	26.6

Plasma arc-method offers not only to reduce the impurity content effectively, but to distribute the alloying element homogeneously. This is very important for producing of electrode materials because of combination of impurity content reduction with desired alloying.

According to demands to impurity content and structure perfection refractory metal and its alloys single crystals are growing by zone refining or plasma-arc methods or by duplex-method which combined consistently both above mentioned methods.

In present investigation W-Re, W-Ir, W-Os-single crystals have been grown by plasma-arc method. Initial material have been produced in form of powder metallurgy rod (as described upper).

Production of perfect W-Re, W-Ir, W-Os-single crystals demanded designation of new growing regimes: electrical parameters of melting, velocity of pull, Ar-He-mixture composition, velocity of seed single crystal rotation.

### Chapter 3. STRUCTURE OF POLY- AND SINGLE CRYSTAL TUNGSTEN ALLOYED BY RARE ELEMENTS

#### 3.1. POLYCRYSTALLINE TUNGSTEN DOPED BY REFRACTORY OXIDES

The thermodynamic properties of the refractory oxides (see Table 3) show that the thorium and yttrium oxides are thermodynamic stable under the conditions similar to the thermal treatment conditions of tungsten-based materials used as cathode materials.

Table 3 Thermodynamic properties of the oxides

Oxide	Melting point, °C	Heat of formation, $-\Delta H_{298}^{\circ}$ kJ/mol	Entropy, $\Delta S_{298}^{\circ}$ J/mol $\times$ deg.	Gibbs' energy, $-\Delta G_{298}^{\circ}$ kJ/mol
ThO <sub>2</sub>	3350	1227	65.2	1169
Y <sub>2</sub> O <sub>3</sub>	2440	1897.3	99.2	1808.5
La <sub>2</sub> O <sub>3</sub>	2320	1789.2	128.1	1698.6

In the W-ThO<sub>2</sub>, W-Y<sub>2</sub>O<sub>3</sub>, W-La<sub>2</sub>O<sub>3</sub> et al. systems, the thermodynamic stable oxide phases, which are formed by the IIIA and IVA group metals (the more electropositive than tungsten), are

in equilibrium with unalloyed tungsten or the tungsten-based solid solution. In these systems, no interactions between the oxides and the tungsten matrix are observed. This fact is confirmed by X-ray microprobe spectrometry data, which show that no diffusion of the impurity elements into the tungsten matrix was found after the high-temperature long-term annealing (at the temperature higher than the oxide melting point).

As was shown by metallography, the oxide particles in initial state are observed as well-edged crystals of 1-10  $\mu\text{m}$  in size. After sintering and welding ( $T = 2550^{\circ}\text{C}$ ), the morphology of the thorium oxide particles does not change (Fig.4); whereas, the yttrium oxide particles turn globular. This fact owes its existence to the partial melting the particles at high temperature (such as  $2550^{\circ}\text{C}$ ) followed by solidification without interaction with the tungsten matrix.

Upon further swaging (the amount of deformation was 25%) at  $1600^{\circ}\text{C}$ , a coarse-grained slightly elongated structure is formed (Fig.5). As was shown by scanning electron microscopy, an average size (diameter) of equiaxial cells is equal to 1.2-1.7  $\mu\text{m}$  in deformed specimens of  $\text{Y}_2\text{O}_3$ -doped tungsten. The inner fields of the cells are virtually free from dislocations, which are mainly concentrated at cell boundaries. The misorientation of the neighbor cells does not exceed  $10-15^{\circ}$ .

The study of recrystallization of the alloys has been carried out on the base of structural changes upon annealing in the temperature range of  $100-2400^{\circ}\text{C}$ . It was found that the recrystallization is a three-stage process.

1. Relaxation of the boundaries of the cells results in the formation of moving boundaries; on this stage, no nuclei of new grains are observed.

2. Breaking-away of low-angle boundaries from the oxide phase particles and their migration, which is accompanied by a formation of subgrains and an increase in their misorientation.

3. Fast growth of comparatively large grains; this process is similar to the collective recrystallization.

Onset recrystallization temperature of the oxide-doped tungsten alloys is higher  $200-250^{\circ}\text{C}$  than that of pure tungsten.

### 3.2. MECHANICAL PROPERTIES OF THE ALLOYS

The particles of the oxide phases significantly affect the plasticity parameters. Dopes of the oxide phases increase an effective elongation, compression, impact strength, because the particles are effective barriers at propagation of the cracks. Increase in the content of the oxide particles is accompanied by the increase in the resistance to failure and results in increase in the brittleness threshold (limit of brittleness).

At high temperatures ( $>250^{\circ}\text{C}$ ), a new deformation mechanism consisting in the formation of micropores around the oxide inclusions is arisen. Increase in the amount of the particles obstructs the propagation of an uniform plastic deformation and increases the tendency to the formation of micronecks. The alloys with minimal content of the particles have the maximal  $\sigma$  and  $\phi$  values at  $T > 250^{\circ}\text{C}$ . Increase in the content of the particles results in decrease in the distance between the particles. When these distances become equal to the particle size, a drastic increase in nucleation of micropores occurs. As the result, the distances between the micropores become very small and micropores joint before the appreciable deformation will take place [11]. It is therefore best to dope the alloys of no more than 1.5-2.0 wt%  $\text{Y}_2\text{O}_3$ .

### 3.3. SINGLE CRYSTALS OF THE W-Re ALLOYS

The single crystals of the W-5wt.% Re alloy have been grown using a plasma-arc melting. Orientation of the single crystal axis coincides with the [110] crystallographic direction. Upon producing the electrodes from these alloys, this orientation of the single crystals allows the best working by turning, griding et al. The W-5 wt% Re alloy rods produced by standard powder technique were used as a start material.

Chemical analysis showed that the single crystals contain from 4.5 to 4.75 wt% Re.

As was found by metallography and X-ray topography, the subgrains are prolonged along the growth direction of the single crystals. Misorientation angles of the subgrain are a  $1-3^{\circ}$ ; sizes of the subgrains are up to a few centimeters along the growth



direction and a few millimeters across (Fig.6).

### 3.4. SINGLE CRYSTALS OF THE W-Os AND W-Ir ALLOYS

The single crystals of the W-2 wt% Os and W-2 wt% Ir alloys were produced by a plasma-arc melting. The orientation of the single crystals coincides with the [110] direction.

The rods of 4 mm in diameter produced by standard powder technique were used as a start material.

A chemical analysis showed that the single crystals contain 1.75 wt% of osmium or iridium.

As was shown by X-ray topography, misorientation of the first order subgrains is  $1-3^{\circ}$ . Sizes of the grain are few cm along the growth direction and few mm across.

As was found by light microscopy, the density of etching pits is equal to  $10^7 \text{ cm}^{-2}$  (Fig.7 and 8). Second order subgrains were found within the first order subgrains; the misorientation of the second order subgrains is no more than  $5-8'$ .

Our investigations showed that the Os- and Re-alloyed tungsten single crystals compare favorably with the Ir-doped tungsten single crystals in perfection. It may be explained by the significant difference in the W and Ir crystallographic parameters as well as in the melting points, that results in the formation of the unequilibrium solidification front.

There are some general features characteristic for the Re-, Ir-, and Os-alloyed tungsten single crystals after the first melting. These are (1) the pores are arranged in the form of concentric circles; (2) the band structure is observed for all single crystals; (3) an increase in the misorientation of the first order subgrains occurs with increasing distance from the seed. For the Ir-alloyed single crystal, this fact may be explained by the above mentioned reasons.

Additions of Os and Ir ruggedize tungsten.

Remelts improve the perfection of the single crystals, but their advisability should be confirmed by the results of model experiments.

#### Chapter 4. EFFECT OF THERMOCYCLING ON THE STRUCTURAL STABILITY AND THE SHAPE STABILITY OF ELECTRODES FROM TUNGSTEN DOPED BY THE REFRACTORY METAL OXIDES

The erosion resistance of the electrode materials is one of the parameters responsible for the service life of the plasma-arc engines. The erosion is caused by sputtering the cathode material, formation of pores, cracks, craters, protrusions on the cathode surface, that results in failure of the plasma-arc engine.

The working end of the electrode is subjected to the most thermal attack as well as to intensive ion and electron bombardment; therefore, there is a need to examine the shape stability of the cathode end and neighbor parts, structure stability, behavior of the activated dopes under the cyclic high-temperature attacks and strong electric fields.

It is known that the working characteristics of the cathodes significantly depends up on the concentration of the activated dopes and their distribution in the surface layer of the tungsten electrode. The thorium diffusion in the surface layers of the Th-doped tungsten cathodes of gas-discharge tubes (lamps) and electrodes working at the high-current charge was studied in [8]. In [12], an electron emission and the diffusion of the thorium atoms from the Th-doped tungsten bulk were studied using an electron projector, and the changes in the thorium concentration in the surface layers, using radiometry. It was found that, before working, thorium presence in Th-doped tungsten mainly as  $\text{ThO}_2$ . On heating to  $2600^\circ\text{C}$  and higher,  $\text{ThO}_2$  reduces to thorium atoms, which diffuse to dislocation aggregates and form the impurity "clouds". From these "clouds", the thorium atoms diffuse through the dislocations to the surface. This process progresses with time, so that, at the moment, only a part of the surface dislocations (from which the thorium atoms have already diffused to the surface) are emission centers. Thereupon, the thorium atoms evaporate and, thus, the emission centers lose their activity. At the same time, the other similar centers arise on the other places, where the thorium atoms have passed through the dislocations. All these processes produce the "flicker" effect of spots on a screen of a plasma fields-emission microscope.

Thorium atoms was found to diffuse also through the grain and subgrain boundaries [13].

Processes occurred in thermoemission cathodes - evaporation, condensation gas absorption, gas evolution, diffusion of the active dope to the surface, and structural recrystallization - are described thoroughly in [2].

The aim of this work is a study of the shape stability and the structural changes in the  $Y_2O_3$ -doped tungsten cathodes used in plasma-arc sets. For the cathodes of the plasma-arc sets such as PD-1, PD-5, working conditions (see Chapter 2) are believed to be similar to the working conditions for the cathodes in the plasma-arc engines.

Thermocycling was carried out using the PD-5 set with a generator of special signals G6-26. Thermocycling conditions and the state of the working ends of the cathodes produced from "BN-15" and tungsten single crystal (without dopes, as comparison) are given in Table 4.

Table 4. Thermocycling conditions and shape stability of various tungsten cathodes

Grade of tungsten	Current, A max	Time, s min	heat- ing	cool- ing	Number of cycles	Total time of thermo- cycling, s	State of cathode business end
BN-15 ( $Y_2O_3$ - doped)	415	85	5	5	300	50	Working state (partial melting)
"--"	415	85	5	5	600	100	Melted
Tungsten single crystal (without dopes)	415	85	5	5	10	1.5	Melted

Studying the cathode surface after work, we can obtain important data on the processes occurred in arc-discharge conditions. Reconstruction of the process run on the cold surface is ambiguous, and so, it is required additional experimental data obtained immediately upon arc discharging.

To examine the subsequent changes in the form of the working ends of the cathodes, a special unit was constructed. The observations of the process were carried out through a special window with up to ten-fold magnification.

When switching on, a unconsolidated ring-shaped scab ("crown") forms on the tungsten cathodes both with dopes and without it. This scab consists of tungsten crystals condensed from the vapor which forms as the result of the tungsten evaporation (Fig.9a). The pure tungsten cathode is partial melt after 10-fold thermocycling (for 1.4 min) and than the failure of the arc is observed (Fig.9b). After 80 cycles, the ring-shaped scab on the  $Y_2O_3$ -doped tungsten cathode consists of isolated partial melt globules. These globules are formed as the result of local evaporation of the dopes, and the cathode begins operate as the pure tungsten cathode (Fig.9c). In this case, unstable arcing is observed.

After 125 cycles, the arcing becomes stable; the second scab containing the partial melt globules is formed (Fig.9d).

The third ring-shaped scab containing such globules is formed after 300 cycles (Fig.9e).

After 480 cycles, the partial melting the second scab is observed (fig.9f).

After 600 cycles, the cathode working end wholly melt; however, a scab is formed at the side. This scab consists of three globules which are arisen as the result of the final diffusion of the dope to the surface (Fig.9g). In this case, the cathode begins to operate similar to the pure tungsten cathode; the arc becomes unstable and arc failure is observed.

Upon studying the cathode surface by a scanning electron microscopy, new data on the surface morphology become available (Fig.10).

After thermocycling, structural changes in the cathode

material were studied on longitudinal sections of the working ends of the cathodes by light microscopy. The structure was observed after etching by the Murokami solution.

The initial structure of the cathodes is fibriform (Fig. 11a). After 300 and 600 cycles, the structure of the oxide-doped and pure tungsten cathodes brings in evidence the directional recrystallization of tungsten by the action of current (Fig. 11, b, c). The recrystallization owes its existence to the preferred growth of the grains with a crystallographic orientation corresponding to the minimal specific electrical resistance and coinciding with the current direction. Because of anisotropy of the heat liberation, the temperature of these grains is higher and they incorporate the colder grains [2].

For the metals having bcc lattices (W, Mo, Ta, Nb), the [100] crystallographic direction is oriented along the current; for the metals with fcc lattices (Ni, Cu, Al), the [110] direction is oriented along the current [14].

These structural changes are characteristic for all tungsten cathodes and are independent of the cathode initial structure, dopes and porosity of the material. The presence of easily ionized dopes increases the cathode temperature (or the diffusion rate of the dope) and prolongs the time of the structural changes in the pure tungsten cathode.

As the dope atoms diffuse to the surface and evaporate, the large grains are formed; the [100] direction of these grains coincides with the current direction.

The found dependences of the directional solidification and the recrystallization of the metals by the action of a current allow to predict the orientation of the working surface of the cathodes (and consequently a work function) on the basis of the lattice type.

#### CONCLUSION

1. Physico-chemical and mechanical properties of tungsten allow to choose this metal as the base of electrode materials for a plasma-arc engine.

2. The most promising alloying components for the tungsten-

based electrode materials are rhenium, iridium, osmium as well as oxides of thorium, yttrium, rare earth metals (mainly of cerium group). These dopes significantly affect the mechanical and emission properties of the electrode materials and, thus, their technological properties. The latter determine yield and arcing parameters which affect reliability and service life of the engine.

3. Increase in the strength of tungsten by alloying with rhenium, iridium, and osmium as well as with the oxides is controlled by a few mechanisms; these are the modification of the structure, the formation of substitution solid solution and blocking the possible plastic shears by the dispersing oxide inclusions. Iridium, rhenium, and osmium yield maximal work function in vacuum and minimal one in vapor of alkali metals. When dissolving in tungsten, these metals will increase its absorption property and emission current of the electrode working in vapor of alkali metals.

Experimental results testify that the thorium and rare earth metal oxides positively affect the emission properties of tungsten, but the mechanism should be clarified.

#### SUMMARY

1. Considering the character of interaction between tungsten and other refractory chemical elements as well as the composition dependence of physico-mechanical properties, determined service parameters of the plasma-arc engine, allow to choose a lot of alloys as the base of the electrode materials; these are W-5 wt%  $\text{ThO}_2$ ; W-2 wt%  $\text{ThO}_2$ -1 wt%  $\text{CeO}_2$ ; W-5 wt% Re-5 wt%  $\text{ThO}_2$ ; W-5 wt% Re-1 wt%  $\text{CeO}_2$ ; W-5 wt% Re-2 wt%  $\text{Y}_2\text{O}_3$ ; W-5 wt% Re; W-2 wt% Os; W-2 wt% Ir.

2. Choosing the alloys, the compositions of which are given in the term 1, we proceeded from their strengthening at the formation of substitution solid solution as well as from hardening action of solid particles. At the same time, we suppose that the alloying additions, being the substitution elements in the solid solutions, and the fine dispersed solid inclusions of the thorium and rare earth metal oxides increase the stability of the emission

properties at the expense of higher stability upon thermocycling, resistance to erosion, high-temperature creep, and attack of the plasma-forming gas components.

3. Creation of the model of plasma arcing under working conditions of the plasma-arc engine allows to decrease a lot of alloys chose as the electrode materials.

4. Two approaches to producing electrode materials are found.

(1) Producing the materials with fine-grained structure, which consists of the tungsten-based solid solutions and oxides inclusions.

(2) Producing the tungsten solid solution-based materials with uniform single crystal structure.

In the first case, the materials are produced by standard powder technique; in the second case, by melting followed by withdrawing the single crystals from the melt.

Each of the approaches has its merits. In the first case, high physical and mechanical properties owe their existence to fine-dispersed structure, chemical composition homogeneity and uniform distribution of the oxide inclusions in a bulk of specimen. The latter are an effective strengthening additions and appreciably determine the emission properties of the material. Moreover, the powder technique offers wide possibilities for producing articles of various shape. In the second case, upon melting, it is impossible to obtain the uniform distribution of the oxide inclusions. Upon withdrawing the single crystal, the inclusions will obstruct the formation of the single crystal structure. Because of, the single crystal materials do not contain the strengthening oxide phase, but they have the other merits concerning the absence of the grain boundaries; these are stability of the properties in the wide temperature range and their orientational dependence, which offers additional possibilities for controlling the properties.

The economic expediency of each of the approaches should be determined by specific problem.

## RECOMMENDATIONS

Tungsten doped by  $\text{ThO}_2$ ,  $\text{CeO}_2$  and  $\text{Y}_2\text{O}_3$  must be used for cathodes of plasma-jet engine. Tungsten single crystals alloyed by Re, Os and Ir must be used for anodes.

To increase the service life of plasma-arc engine, it is necessary to improve the composition and the structure of the electrode materials. For this purpose, the detail analysis of behavior of active dopes and structural changes in electrodes should be carried out.

The final conclusion on the expediency of use of these materials and on the development of methods of their improving may be reached after full-scale experiments followed by the analysis of the surface morphology and the structure of the electrodes (especially the electrode working end).



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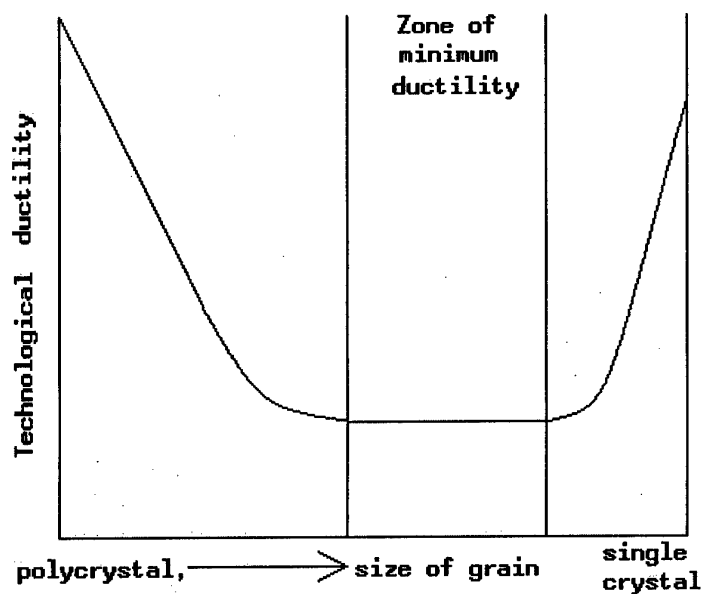


Fig.1. Ductility of tungsten as a function of grain size

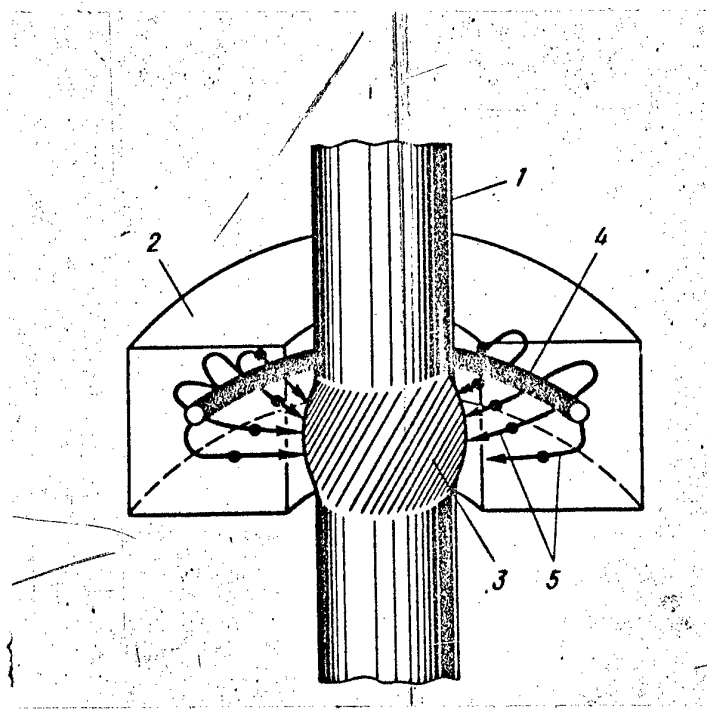


Fig.2. General scheme of electron-beam zone-refining method used to grow single crystals of refractory metals and alloys: 1 - sample (anode); 5 - electrones; 3 - melting zone; 4 - cathode

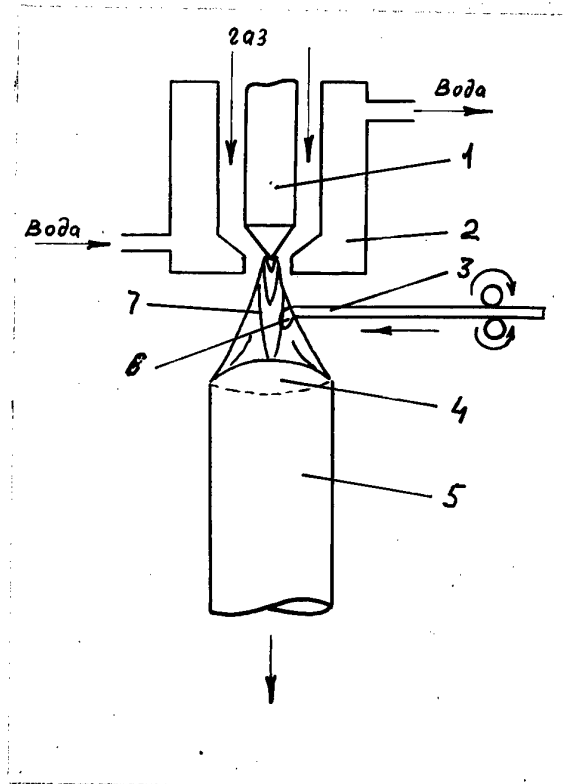


Fig.3. General scheme of plasma-arc method used to grow single crystals of refractory metals and alloys

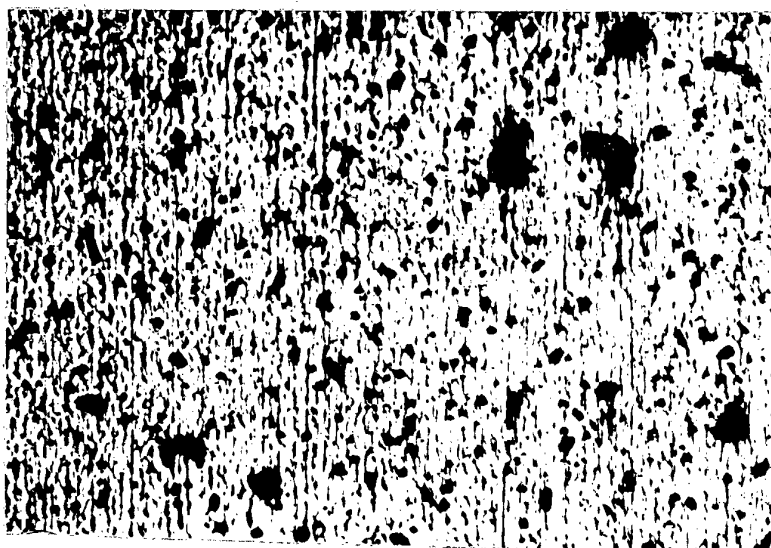


Fig.4. External appearance of the hollows and  $\text{ThO}_2$ -particles in W-5 wt%  $\text{ThO}_2$ -cathode (light optical microscopy, x500)

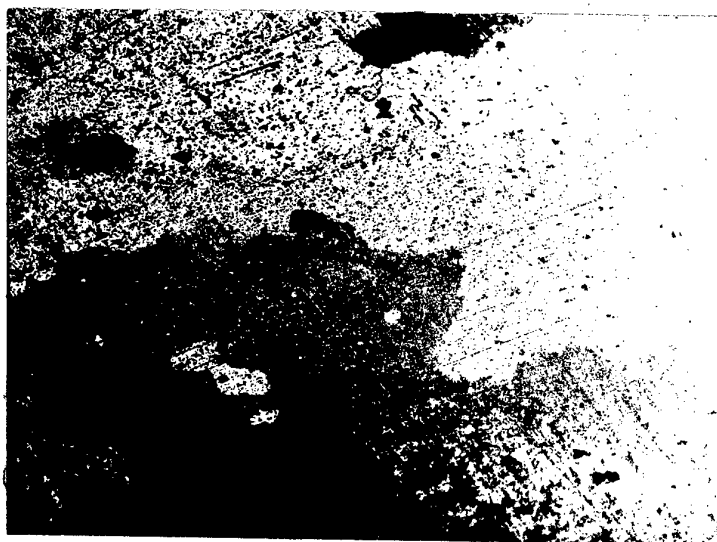


Fig.5. Microstructure of W-5 wt%  $\text{ThO}_2$ -cathode (light optical microscopy, x200)

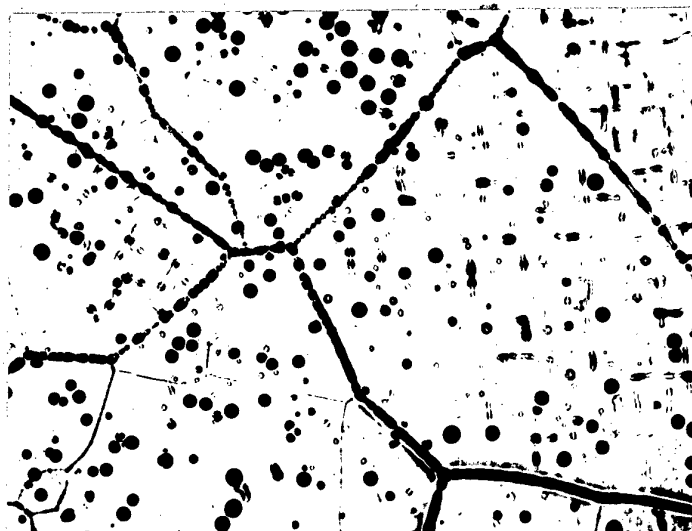
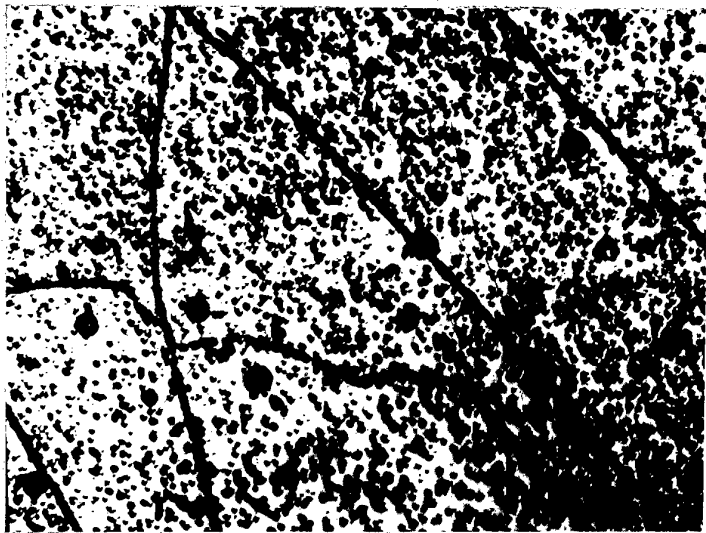


Fig.6. Microstructure of W-Re (100) single crystal: a,b - bottom of single crystal; c,d - top of single crystal (a and c - light optical microscopy, x500; b and d - X-ray topography)



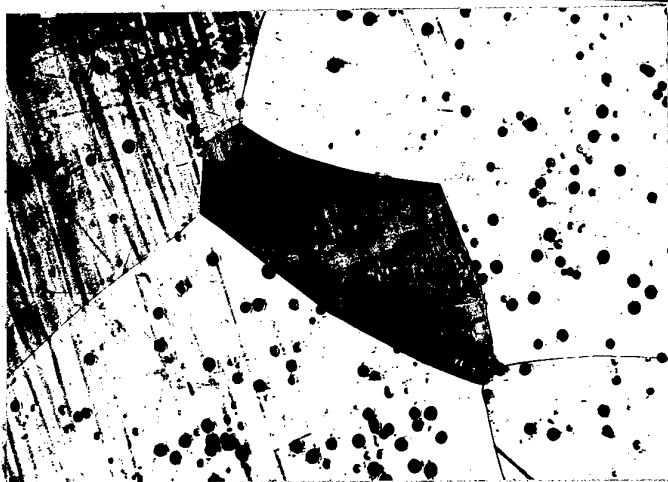
a



b



c



d

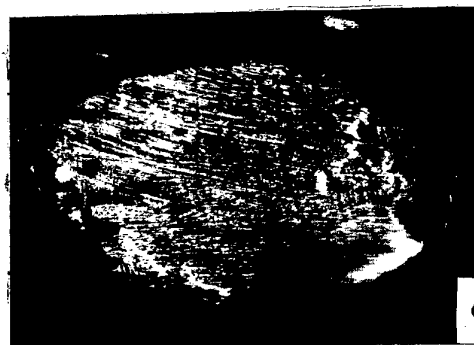
Fig.7. Microstructure of W-Os (100) single crystal: a,b,c - bottom of single crystal (a,b - light optical microscopy, x50 and x500); c - X-ray topography); d - top of single crystal (light optical microscopy, x50)



a



b



c



d

Fig.8. Microstructure of W-Ir (100) single crystal: a,b,c - bottom of single crystal (a,b - light optical microscopy, x50 and x500); c - X-ray topography); d - top of single crystal (light optical microscopy, x50)



a



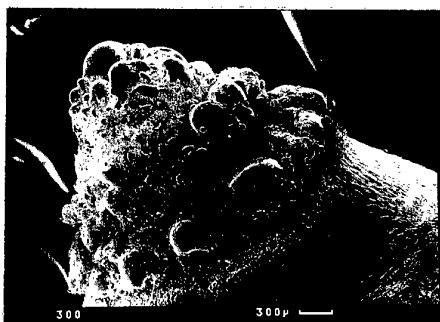
b



c



d



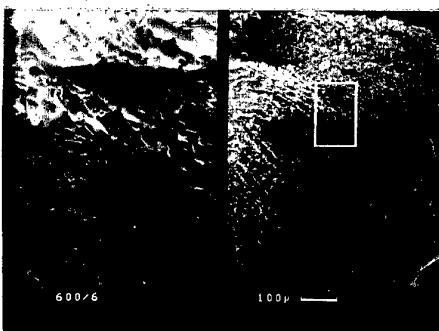
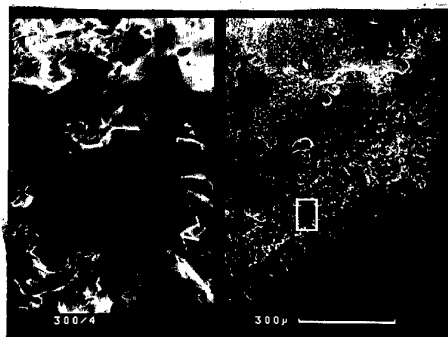
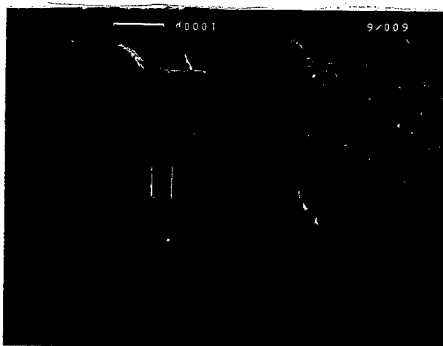
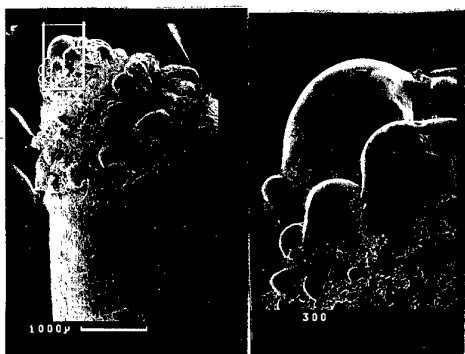
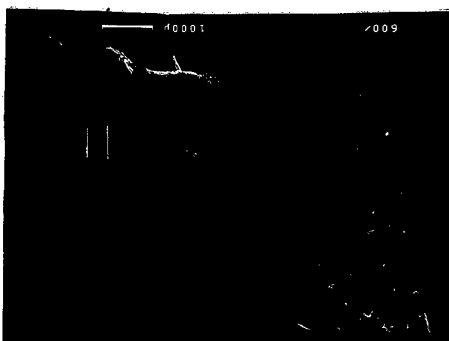
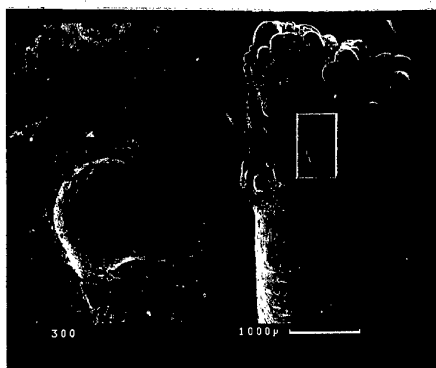
300 300μ



500 500μ

Fig.9. External appearance of W-2 wt%  $Y_2O_3$ -cathode bus end after different number of thermocycling.





after 300 thermocycles

after 600 thermocycles

Fig.10. Surface morphology of W-2 wt%  $Y_2O_3$ -cathode bus end after thermocycling (electron scanning microscopy):

transient zone  
after 600 thermoc.

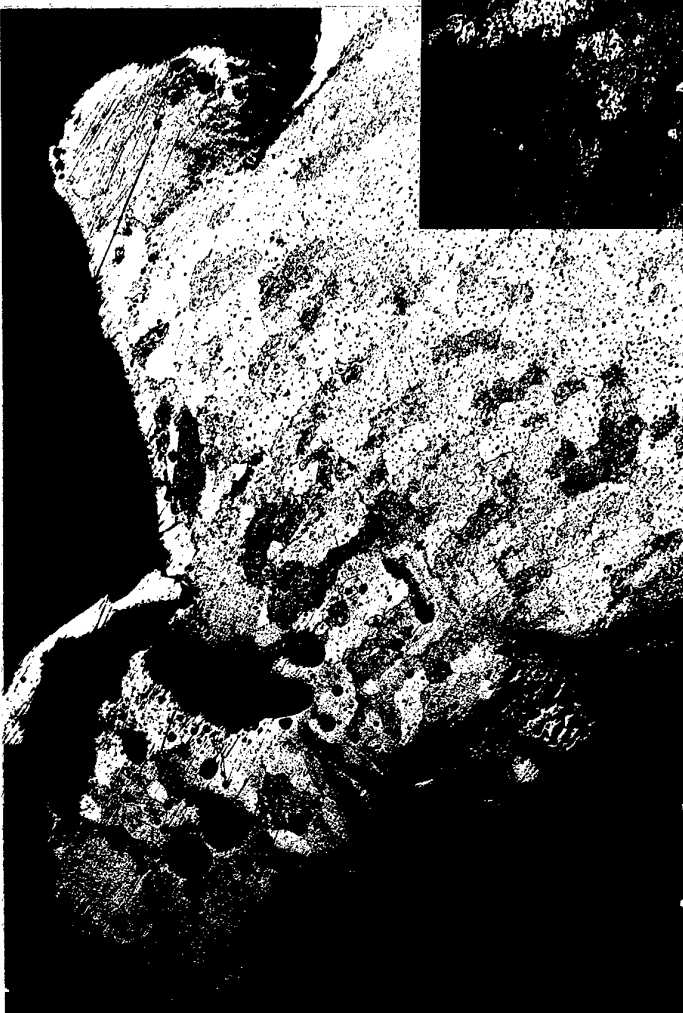
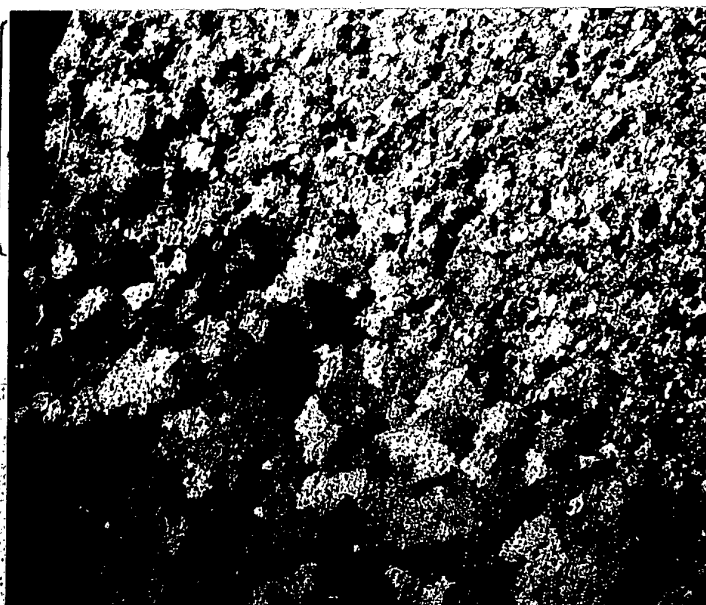


Fig.11. Microstructure of W-2 wt%  $Y_2O_3$ -cathode business end before thermocycling (a), after 300 (b) and 600 (c) thermocycles: (light optical microscopy: x50)